Understanding Mercury Mobility at the Carson City Superfund Site, western Nevada, USA: Interpretation of Mercury Speciation Results from Mill Tailings, Soils, and River and Reservoir Sediments

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Introduction

The milling of gold and silver ores from the Comstock lode in west-central Nevada, USA, largely between 1860 and 1900, released approximately 7,000 tons of Hg to the Carson River/Lahontan Reservoir system. This magnitude of contamination, and the realization that Hg is bioaccumulating in fish, resulted in the Carson River area being named a Superfund Site in 1990.

Systematic spatial changes in the speciation of Hg from source to sink elucidate the processes governing the movement and fate of Hg in the system. Further, the speciation of Hg influences potential remediation scenarios and the potential for Hg to enter groundwater.

Features of published methods of determining the speciation of Hg in sediments and soils were combined to produce a technique which appears to reliably estimate the proportions of discrete Hg species in samples from the Carson River Superfund Site.

Methodology

After a careful review of the literature covering the determination of various species of Hg in solid samples the following method was established (based partially on the work of Eaganhouse et al.(1978), Di Giulio and Ryan (1987), and Quevauviller et al.(1992):

1. Place 10.000 g sample in 250 ml beaker, add 5 ml HNO_3 and 15 ml HCl, cover with watch glass, gently boil for 45 minutes, dilute to 50 ml with 3N HCl, and determine *total Hg* by cold vapor atomic absorption spectrometry (CV-AAS).

2. Place 10.000 g sample in a 250 ml borosilicate beaker and heat in a drying oven for 48 hours at 180°C. Determine Hg content of heated sample and compare to total Hg content of sample; difference is *elemental Hg*.

3. Using sample residue from step 2., add 50 ml 0.5 M $MgCl_2$, mix at room temperature for 2 hours, let stand for 60 minutes, decant 40 ml, centrifuge, determine *exchangeable Hg* by CV-AAS.

4. Using sample residue from 3., add 50 ml 5 % (v/v) HCl, mix at room temperature for 2 hours, let stand 60 minutes, decant 40 ml, centrifuge, determine *strongly-bound Hg* by CV-AAS.

5. Using sample residure from 4., add 25 ml 0.2 N NaOH, mix at room temperature for 2 hours, add 25 ml 4 % (v/v) CH_3COOH (glacial acetic acid), let stand 60 minutes, decant 40 ml, centrifuge, determine *organic Hg* by CV-AAS.

6. Subtract *elemental Hg, exchangeable Hg, strongly-bound Hg,* and *organic Hg* from *total Hg,* difference is *residual Hg.* Residual Hg could be Hg encapsulated by silica or Hg sulfide; at the Carson River Superfund Site all residual Hg is considered to be *Hg sulfide.*

Sampling and Analysis

Samples were collected from the upper 5 to 10 cm of sediment from the active channel of the Carson River and Lahontan Reservoir. The upstream sample was collected from a location above which mercuriferous tailings are judged to be entering the Carson River and thereby constitutes a background sample. The next four samples were collected from 8 to 58 km downstream in the river and the final sample was collected from Lahontan Reservoir, 12 km more distant (Figure 1). The samples were placed in plastic bags and refrigerated until analysis. Wet samples were used for analysis and moisture content was determined on a separate sample split; all analytical results were then corrected to a dry basis (105 to 110°C).
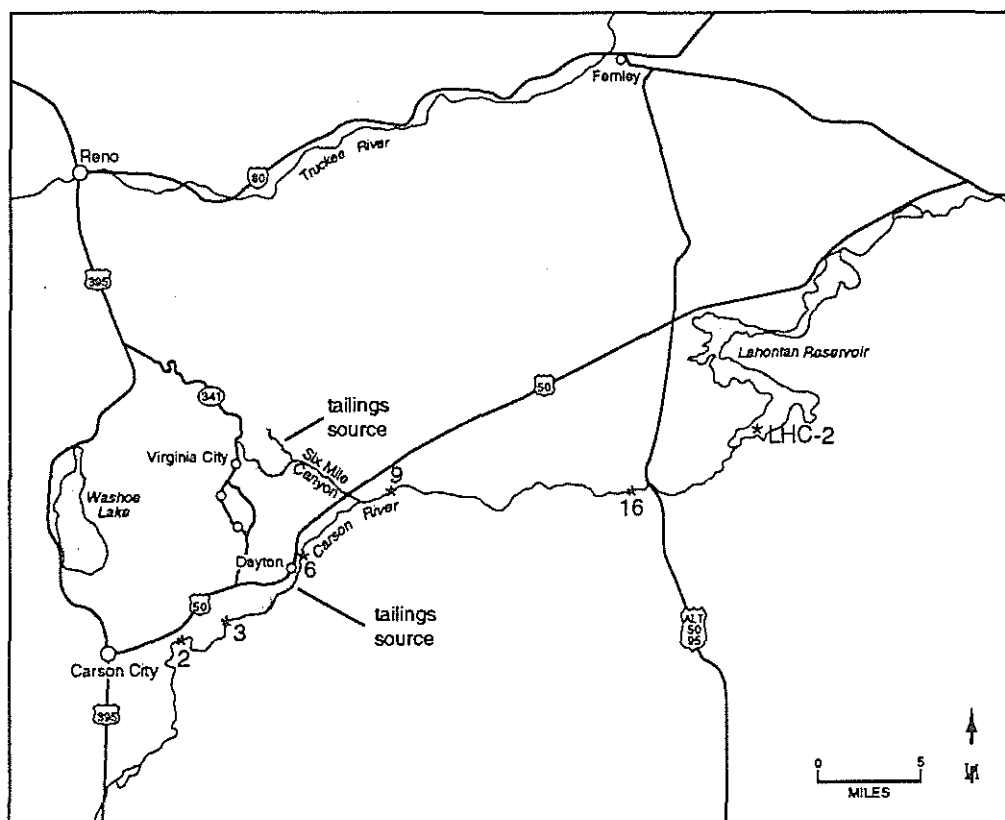

Figure 1. Map of Carson River Superfund Site showing sample locations and source areas of mercuriferous mill tailings.

Results

Total Hg contents of river/reservoir sediments show a steady increase downstream as contaminated materials enter the active channel, mainly from tailings being eroded from banks as the river meanders through its floodplain (Figure 2).

The proportion of elemental Hg in these samples starts near zero in the upstream sample at 22 km, increases to greater than 90 % at 29 km where the influence of mercuriferous mill tailings is seen (>95 % elemental Hg), the proportion degrees down-river, and decreases sharply in the reservoir sample (Figures 1 and 2). In the Carson River samples the proportion of exchangeable Hg varies inversely with respect to elemental Hg and then both species decrease sharply in the Lahontan Reservoir sample. This relationship is thought to reflect the slow dissolution of elemental Hg with re-adsorption of the released Hg onto clays, organic matter, iron and manganese oxides, and other fine particles with high surface charges. This interpretation is supported by the observation that the Hg/Au of river sediments increases downstream as Hg is selectively dissolved out of upstream amalgam particles and becomes attached to fine particles which are deposited in downstream areas.

Organic Hg distribution is similar to exchangeable Hg. While the upstream sample at 22 km contains very low total Hg (29 ppb), the majority of this Hg is related to organic matter and exchangeable particle sites in the sediment. Five percent or less of the Hg in the downstream samples is related to the small amount of organic matter present (0.1 % or less organic C).

The proportion of residual Hg in these samples is generally less than 10 % except in the sample from Lahontan Reservoir which contains 36 % residual Hg. In this system residual Hg is probably Hg sulfide, produced in situ where sulfate reducing bacteria enhance the activity of sulfide sulfur in the sediments. It is reasonable that the low energy, more anoxic reservoir environment would be conducive to higher reduced sulfur activity.

Additional speciation analyses of vertical soil profiles containing Hg-contaminated tailings indicate fixation of downwardly migrating Hg as Hg sulfide in the deepest, most anoxic portion of the profile (compatible with speciation observations in the river/reservoir samples). This is compatible with measurements of Hg in groundwater which has not been found to exceed the EPA limit of 2 ppb for drinking water. The shallowest soil horizons are characterized by the highest proportions of organic and exchangeable Hg, indicating upward transport of Hg, probably as vapor and/or through capillary action of vadose water.

References Cited

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Figure 2. Downsteam trends in Carson River Hg species.